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**PHYSICAL PROPERTIES AND CHEMICAL ANALYSES OF
ELECTROLYTES FOR SEALED SILVER-ZINC BATTERIES**

A. H. Reed, E. A. Roeger, Jr., A. Fleischer, and J. McCallum

Battelle Memorial Institute
Columbus Laboratories

TECHNICAL REPORT AFAPL-TR-69-47

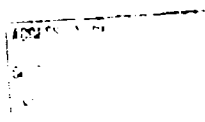
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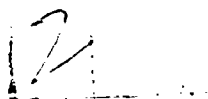
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**"PHYSICAL PROPERTIES AND CHEMICAL ANALYSES OF
ELECTROLYTES FOR SEALED SILVER-ZINC BATTERIES"**

A. H. Reed, E. A. Roeger, Jr., A. Fleischer, and J. McCallum

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FOREWORD

This report describes work performed at the Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio, by personnel of Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio, under Contract AF 33(615)-3701. The Budget Sequence No. is 6(638173 62405212).

This report was submitted by the authors in April 1969 and covers work done during the periods July 1966 to April 1967 and October 1968 to March 1969.

The cognizant Air Force scientist is APIP-1 Mr. Gerald H. Miller, Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio. His attention to this work has helped to direct the work toward the particular interests of the United States Air Force.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

CURTIS KELLY, Chief
Energy Conversion Branch
Aerospace Power Division

ABSTRACT

Electrolytes for sealed silver-zinc batteries have been analyzed for KOH, ZnO, K_2CO_3 , and Ag_2O at -25, 0, 25, and 40 C. In such electrolytes the solubility of Ag_2O is of the order of 10^{-6} N compared to 10^{-4} N in pure KOH electrolytes. The addition of K_2CO_3 while keeping the potassium ion concentration constant decreases the solubility of ZnO. These solutions require about 200 hours to reach steady state conditions. The conductivity of the electrolyte is decreased by the addition of ZnO. When 40 percent KOH is saturated with ZnO its conductivity is decreased to about 80 percent of the conductivity of pure 40 percent KOH. The addition of K_2CO_3 , while keeping the potassium ion concentration constant, further decreases the conductivity. The density of ZnO-saturated 40 percent KOH solutions shows that the volume of such a solution can be obtained by considering the volumes of solid ZnO and 40 percent KOH to be additive. The freezing points of ZnO-saturated 40 percent KOH solutions containing varying amounts of K_2CO_3 were found to be similar to that of pure 40 percent KOH; namely -37 C. Extreme instances of supercooling were observed in which solidification sometimes did not occur at -65 C.

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PHYSICAL PROPERTIES AND CHEMICAL ANALYSES OF ELECTROLYTES FOR SEALED SILVER-ZINC BATTERIES

by

A. H. Reed, E. A. Roeger, Jr., A. Fleischer, and J. McCallum

INTRODUCTION

A knowledge of the physical and chemical properties of electrolytes used in silver-zinc batteries is an important step toward understanding the operation of such batteries. An understanding of the properties of the electrolyte and the role it plays in successful battery operation could benefit both users and manufacturers of silver-zinc batteries.

The work described in this report is a study of electrolytes typical of those found in silver-zinc storage batteries. The electrolyte is usually a 40 percent KOH solution to which ZnO may have been added. During use, varying quantities of K_2CO_3 and Ag_2O will become dissolved in the electrolyte. Such an electrolyte, actually found in batteries, is thus quite different from a pure 40 percent KOH solution. Therefore, measurements which will have real meaning in regard to battery electrolytes must be made on electrolytes which contain the additional components besides KOH. The literature contains a number of studies on the solubility of Ag_2O in pure KOH solutions which do not agree among themselves.

The major purpose of this report is not to resolve the variation in literature data on the solubility of Ag_2O in KOH, but to show that ZnO and K_2CO_3 in the electrolyte have an effect on the solubility of Ag_2O and other properties of electrolytes for silver-zinc batteries.

The experimental portion of the silver oxide solubility studies was separated into two parts which were performed about 20 months apart. Plans for the first part were in line with a common research strategy to make measurements on the simplest systems under carefully controlled conditions. As reproducible and meaningful results were achieved, the next step would be to introduce one more variable but, again, under carefully controlled conditions. When dependable results were achieved, a third variable could be introduced into the experiments. Finally, when the effects of all variables were understood, decisive measurements could be made in actual battery electrolytes.

The second part started with an electrolyte that might be found in a silver-zinc cell after reaching a steady state with partially charged electrodes. Carbonate was then introduced in a series of experiments to simulate electrolytes actually existing in batteries. A few control measurements were to be made for the purpose of showing that the data could be related to data in the literature.

REVIEW OF INFORMATION ON SILVER OXIDE SOLUBILITY

The oxides of silver are sparingly soluble in neutral and alkaline solutions. At room temperature the maximum solubilities are of the order of 5×10^{-4} molar in water and KOH solutions. The low solubilities have several consequences for physical chemical studies of aqueous alkaline-silver oxide systems. Analytical procedures must be capable of desired accuracy at low concentrations of silver compounds. Another consequence of low solubility is that small amounts of impurities can have a large effect on the experimental results. This, in turn, introduces the further analytical problem of detecting and identifying impurities. The discrepancies in equilibrium data reported by various workers may be caused by undetected impurities that interfere with the analytical procedures.

The Silver Oxides

The most common silver oxide is that of monovalent silver, Ag_2O . Another oxide which is encountered in all silver-zinc cells is expressed by the stoichiometric formula AgO . The valency of the silver in AgO is still debated, and the existence of still higher oxides in a stoichiometrically pure state will be discussed later.

Ag_2O is a brownish-black crystalline solid. It is thermodynamically stable in air to above 100 C. At 25 C, the equilibrium partial pressure of O_2 from

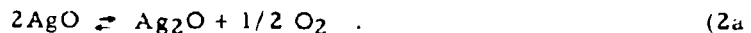


as calculated from the free energy of formation of $\text{Ag}_2\text{O}^{(1)}$, is about 10^{-4} atm. Ag_2O is usually prepared by precipitation from a solution of a soluble silver salt (frequently nitrate) with a hydroxide solution. For some studies, barium hydroxide is substituted for the alkali metal hydroxide in this preparation to prevent formation of Ag_2CO_3 . The oxide can also be prepared by direct oxidation of the metal at 200 C, with oxygen under pressure, or by anodic oxidation of silver in an alkaline solution. The potential must not be allowed to go above the potential for the formation of Ag_2O .

The only higher oxide of silver which has been established as existing for any extended time in the solid state is AgO (or, equivalently, Ag_2O_2). This oxide is not thermodynamically stable in air over the temperature range of operation of silver-zinc cells (-40 C and up). At 25 C, the equilibrium pressure of O_2 for



calculated from the free energy of formation of $\text{AgO}^{(1)}$, is about 10^4 atm. In the presence of KOH, AgO decomposes to Ag_2O according to



The equilibrium partial pressure of oxygen calculated from free energy of formation data at 25 C⁽¹⁾ for reaction (2a) is about 10^{11} atm. The rate of decomposition of Ag₂O at room temperature in air and water is low enough so that it can be stored and handled without difficulty. Ag₂O may be prepared in the laboratory by anodic oxidation of Ag₂O in an alkaline solution. Other methods of preparation rely on oxidation of Ag⁺ in solution by oxidizing agents such as ozone and peroxydisulfate.⁽²⁾

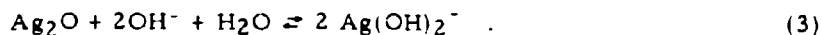
The actual valence of silver in Ag₂O apparently is not +2 but a mixture of +1 and +3. Scatturin, et al,⁽³⁾ concluded from neutron diffraction measurements that there are equal amounts of two types of silver in Ag₂O corresponding to Ag⁺ and Ag³⁺. Their conclusion is in concurrence with the observed diamagnetism of Ag₂O, a property which is incompatible with the presence of Ag²⁺ with its unshared electron.

Many claims have been made for the existence of higher oxides of silver in the solid state. Casey and Moroz⁽⁴⁾ mention that about 100 papers deal with the subject. Both Casey and Moroz⁽⁴⁾ and Burbank and Wales^(5, 6) question the evidence for existence of such oxides. Both groups were specifically concerned with claims of electrolytically formed Ag₂O₃. Other methods claimed for preparation of the trivalent oxide almost surely result in inclusion of other ions in the crystal, giving such compounds as (Ag₃O₄)₂·AgNO₃, (Ag₃O₄)₂·AgF, and (Ag₃O₄)₂·AgSO₄.⁽⁷⁾

Burbank and Wales made X-ray diffraction studies of a freshly formed silver oxide surface at 23-26 C in 35 percent KOH. They found no evidence for any oxides other than Ag₂O and Ag₂O. On the other hand, Casey and Moroz worked in eutectic KOH-H₂O (about 30 percent KOH) at -40 C to minimize the decomposition rate of any higher oxides. By analysis of potential decay, temperature coefficients of decomposition rates, and polarization curves, they concluded that a layer of Ag₂O₃ up to 70 molecular layers thick is formed. Thus, there is evidence of Ag₂O₃ at low temperatures. A recent paper⁽⁴⁰⁾ has reported the formation of Ag₂O₃ at 200-300 C in the presence of ethylene and oxygen.

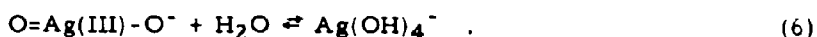
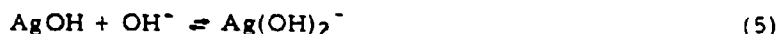
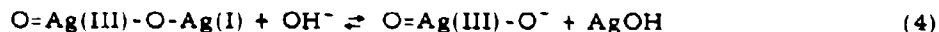
The Solution Species for Silver Oxides

Johnston, Cuta, and Garrett⁽⁸⁾ and Laue⁽⁹⁾ carried out careful and systematic studies of the nature of the solution species for Ag₂O-KOH(aq). They concluded on the basis of solubility measurements of Ag₂O in a range of alkaline solutions that AgO⁻ was the dominant species. Pleskov and Kabanov⁽¹⁰⁾ considered this conclusion erroneous and in turn proposed that multinuclear complexes, predominantly [Ag₃O(OH)₂]⁻, existed in alkaline solutions. They based their conclusion on results of potentiometric measurements. Sillen, et al,⁽¹¹⁾ used a distribution method and potentiometric measurements to reach the conclusion that no polynuclear species were present. They concluded that Ag(OH)₂⁻ is the silver species in alkaline solution. This hydrated form, which is equivalent to AgO⁻, is the preferred representation in aqueous solutions when no evidence for other forms exists.⁽¹¹⁾ Sillen, et al, do suggest that, in strongly alkaline solutions, Ag(OH)₃⁻ may occur. The presently accepted formula thus is Ag(OH)₂⁻, and the dissolution process is represented by

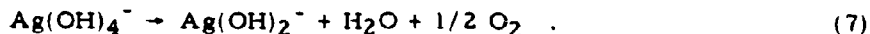


Amlie and Ruetschi⁽¹²⁾ used a polarographic technique to compare the ionic species introduced into 30 percent KOH by Ag₂O and Ag₂O. Their results gave no indication of

the presence of dissolved divalent silver. They concluded that any divalent silver species decompose rapidly and give data on rates of oxygen evolution from AgO in KOH solutions. Attempts by McMillan⁽¹³⁾ to observe paramagnetic resonance of solutions of AgO in KOH support Amlie and Ruetschi's conclusions. If a complex such as $\text{Ag}(\text{OH})_3^-$ were present in alkaline solutions, it should exhibit paramagnetic resonance because it has an odd number of electrons. No paramagnetism could be found in 1 N KOH solutions saturated with AgO and frozen. McMillan then suggests a scheme for AgO dissolutions in alkaline media:



To account for Amlie and Ruetschi's results, the rapid decomposition process would then be represented as:



This scheme for the dissolution of AgO yields the same specie, $\text{Ag}(\text{OH})_2^-$, as is obtained from the dissolution of Ag_2O according to Equation (3).

Fleischer⁽¹⁴⁾ has shown that the solubility of AgO in KOH solutions can be interpreted as corresponding to the solubility of a mixture of AgO and Ag_2O , since AgO loses oxygen in the presence of KOH to form Ag_2O . The phase rule requires that the activity of the soluble silver species be fixed at a given temperature and KOH concentration. Thus, it may be concluded that the activity of soluble silver species produced by the dissolution of AgO must be the same as produced by dissolution of Ag_2O .

Solubility of Ag_2O in KOH Solutions

Results of six* different investigations of silver oxide solubility in alkaline solutions are available in the literature. (15, 10, 12, 8, 16, 9) The results for 25 C are summarized in Table I and Figure 1 for KOH solutions and in Table II and Figure 2 for NaOH solutions. It is quite apparent that differences exist in the data above 6 N KOH. An examination of the materials used, the experimental conditions and the analytical procedures has revealed no obvious reason for the differences. A summary of the experimental conditions and procedures of the various workers is given in Table III.

Dirkse⁽¹⁶⁾ made several studies of the decomposition of silver species in solution. He found initially high solubility values which decreased with time. The values reported by him are not the highest he observed but are the ones recorded after more than a day. Dirkse's experiments will be discussed further in the section on rates of dissolution.

*According to one recent review note [T. J. Gray and R. Eiss, *Nature*, **194**, 469 (1962)], a seventh group, Mathur and Dahr, also studied Ag_2O solubility in KOH. A careful check of the reference revealed data for Ag_2O in water only. The data tabulated by Gray and Eiss are all taken from Laue⁽⁹⁾ and Johnston, Cuta, and Garrett⁽⁸⁾ and are for NaOH, not KOH.

TABLE I. SOLUBILITY OF Ag_2O IN KOH

| | <u>N KOH</u> | <u>N $\text{Ag}(\text{OH})_2^-$</u> |
|--|--------------|--|
| Pleskov and Kabanov ⁽¹⁰⁾ , 25 C, | 3 | 3.8×10^{-4} |
| rotating disk, diffusion coefficient, | 6.5 | 5.2 |
| Pyrex, N_2 atm | 15 | 6.7 |
| Kovba and Balashova ⁽¹⁵⁾ , | 1 | 2.2×10^{-4} |
| 25 C, | 5 | 5.0 |
| radiotracer, | 10 | 6.0 |
| glass, 50 C | 10 | 8 |
| 78 C | 10 | 24 |
| Amlie and Ruetschi ⁽¹²⁾ , 25 C, | 0.95 | 1.7×10^{-4} |
| potentiometric, Pyrex, N_2 atm | 1.9 | 3.0 |
| | 4.2 | 4.5 |
| | 5.7 | 4.8 |
| | 7.0 | 4.7 |
| | 8.3 | 4.6 |
| | 9.6 | 4.5 |
| | 11.3 | 4.2 |
| | 13.4 | 3.4 |
| Johnston, Cuta, and Garrett ⁽⁴⁾ , 25 C, | 0.014 | 0.061×10^{-4} |
| potentiometric, Pyrex, N_2 atm | 0.021 | 0.063 |
| | 0.025 | 0.074 |
| | 0.031 | 0.088 |
| | 0.046 | 0.107 |
| | 0.060 | 0.145 |
| | 0.083 | 0.177 |
| | 0.12 | 0.256 |
| | 0.17 | 0.355 |
| | 0.41 | 0.796 |
| | 0.67 | 1.20 |
| | 1.63 | 2.76 |
| | 2.06 | 3.18 |
| | 3.01 | 3.87 |
| | 3.61 | 4.25 |
| | 5.01 | 4.70 |
| | 5.24 | 4.88 |
| Dirkse ⁽¹⁶⁾ , 25 C, potentiometric | 6.9 | 3.69 |
| | 10.0 | 2.83 |
| | 11.7 | 2.43 |
| 10 C | 6.9 | 2.98 |
| | 10.0 | 2.53 |
| | 11.7 | 2.35 |
| 0 C | 6.9 | 2.22 |
| | 10.0 | 1.87 |
| | 11.7 | 1.70 |

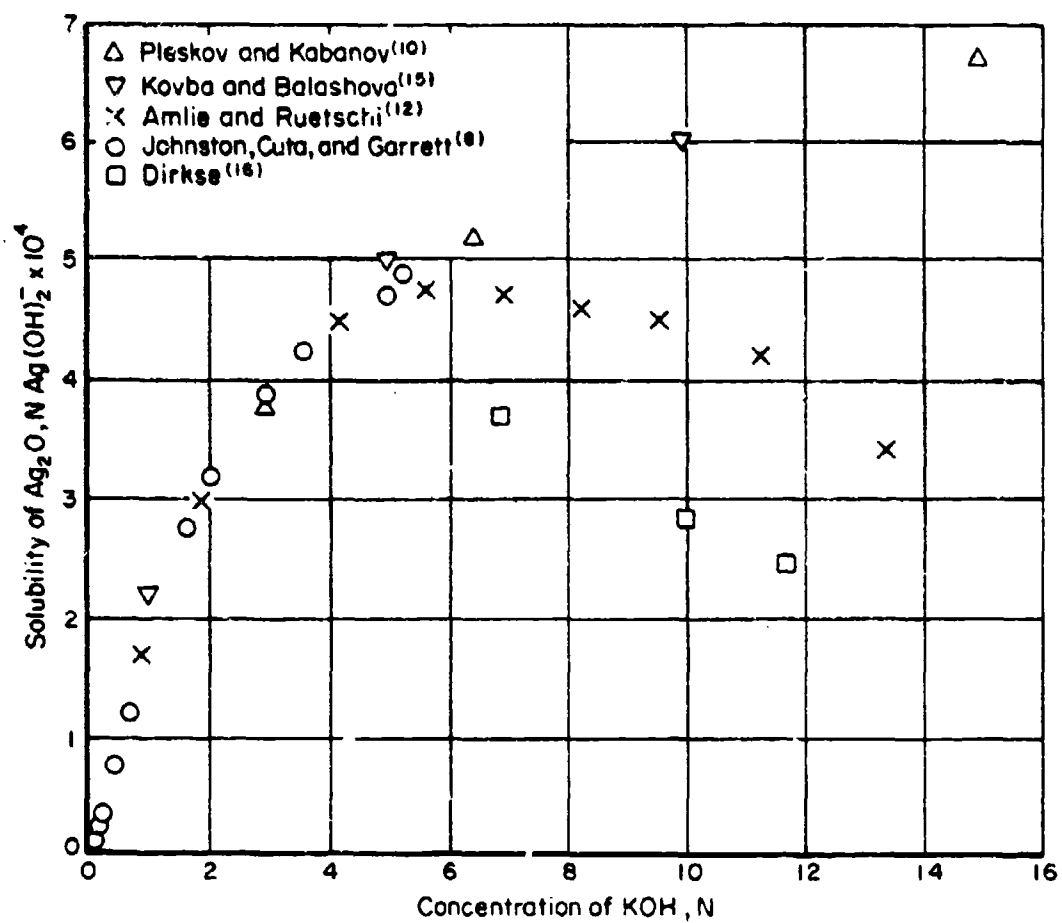


FIGURE 1. SOLUBILITY OF Ag_2O IN AQUEOUS KOH

TABLE II. SOLUBILITY OF Ag_2O IN NaOH

| | <u>N NaOH</u> | <u>N $\text{Ag}(\text{OH})_2^-$</u> |
|--|---------------|--|
| Johnston, Cuta, and Garrett ⁽⁸⁾ | 0.012 | 0.055×10^{-4} |
| | 0.020 | 0.065 |
| | 0.022 | 0.067 |
| | 0.039 | 0.097 |
| | 0.051 | 0.11 |
| | 0.057 | 0.13 |
| | 0.075 | 0.18 |
| | 0.089 | 0.20 |
| | 0.12 | 0.26 |
| | 0.15 | 0.35 |
| | 0.18 | 0.36 |
| | 0.21 | 0.41 |
| | 0.27 | 0.52 |
| | 0.39 | 0.74 |
| | 0.40 | 0.73 |
| | 0.75 | 1.47 |
| | 0.78 | 1.53 |
| | 1.17 | 1.99 |
| | 1.28 | 2.25 |
| | 1.39 | 2.36 |
| | 1.86 | 3.12 |
| | 2.33 | 3.60 |
| | 2.51 | 3.49 |
| | 2.76 | 4.34 |
| | 3.22 | 4.05 |
| | 4.89 | 4.79 |
| | 6.60 | 5.43 |
| Laue ⁽⁹⁾ , 25 C, potentiometric Jena glass | 0.01 | 0.09×10^{-4} |
| | 0.10 | 0.29 |
| | 0.51 | 0.90 |
| | 1.02 | 1.58 |
| | 1.04 | 1.63 |
| | 1.05 | 1.42 |
| | 1.06 | 1.68 |
| | 2.26 | 3.09 |
| | 5.13 | 4.32 |
| | 5.34 | 5.08 |

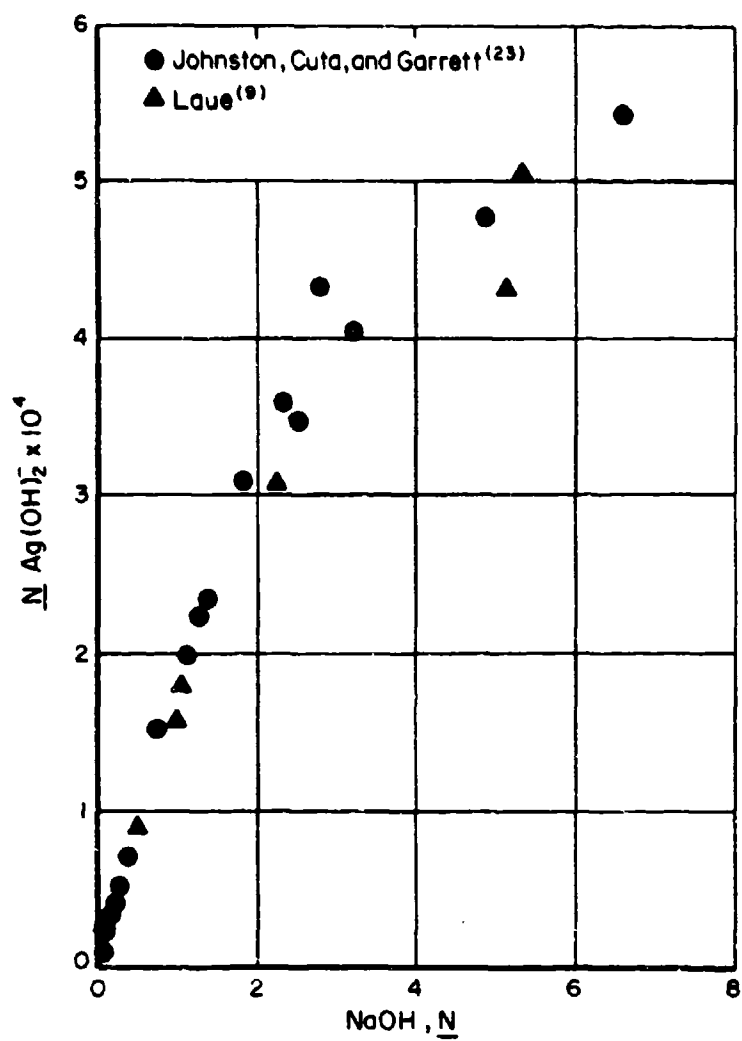


FIGURE 2. SOLUBILITY OF Ag₂O IN NaOH AT 25 C

TABLE 1.3 MATERIALS, EXPERIMENTAL CONDITIONS, AND PROCEDURES USED TO DETERMINE SOLUBILITY OF Ag_2O IN ALKALINE SOLUTIONS

| Investigators | Material Source | | Equilibration | | | Analytical | |
|---|-------------------------------|-------------------------------------|-----------------------------------|-----------------------|--------------|----------------------------------|--|
| | Ag_2O | Alkali | Protective Atmosphere | Vessel | Time | Filter Material | Analysis Method |
| Laue ⁽³⁾ | $AgNO_3$ † $Ba(OH)_2$ | Solid NaOH (Merck) | None, flasks sealed with paraffin | Jena glass | 1-6 hours | Schott glass | Electrodeposition from ammoniacal solution |
| Johnson, Cuta, and Garrett ⁽⁸⁾ | $AgNO_3$ † $Ba(OH)_2$ | K or Na Amalgam Decomposition | N_2 , flasks sealed | Pyrex | 10-22 days | Glass (0.01-0.4N) Silver (>0.4N) | Potentiometric titration with KI |
| Pleskov and Kabanov ⁽¹⁰⁾ | Not specified | Not specified solution electrolysed | N_2 | Pyrex or Schott glass | Several days | Not used | Rotating disk polarography |
| Kovha and Balashova ⁽¹⁵⁾ | $AgNO_3$ | C. P. KOH solution electrolysed | N_2 | Glass | 70-80 hours | Not mentioned | Radioactive tracer, Ag^{110} |
| Amlic and Ruetschi ⁽¹²⁾ | Purified Ag_2O Mallinckrodt | Fisher certified pellets | Not specified | Not specified | 3-4 weeks | Pyrex | Potentiometric titration with KI |
| Dirkse ⁽¹⁶⁾ | Commercial | Not given | Not specified | Not specified | 1 day | Pyrex | Potentiometric titration with KI |

The solubilities in NaOH up to 6 N are the same as those for KOH within the limits of experimental error, as seen from Figures 1 and 2. The region of concentration above 6 N KOH is of greatest interest in battery technology, so it is important to find out the reason for the discrepancies.

The use of three different analytical procedures for silver by the four investigative groups, with a resulting close agreement at low alkali concentrations, does not completely eliminate the possibility of some methodical error inherent in a method. It is possible that all methods of analysis will give values for the solubility of Ag₂O which are in agreement when the concentration of KOH is low. As the concentration of KOH becomes higher, however, the relative errors of the methods may become different so that one method may consistently give values of Ag₂O solubility that are too high or too low in the presence of a high KOH concentration.

Two factors which investigators have claimed to be particularly careful about are the presence of colloidal silver oxide and the presence of oxidizable materials. By careful treatment of solutions and apparatus, organic reducing agents were said to be eliminated. Colloidal material was observed in the filtrate in two of the studies, but the good agreement of results below 6 N KOH suggests the elimination of colloidal material as a major contributor to the silver analytical values below 6 N KOH, even though colloidal silver could contribute to differences in the more concentrated solutions. At the present time, there is insufficient data in the literature to resolve the discrepancies reported in silver oxide solubility in concentrated KOH solutions.

Effect of ZnO

The effect of zinc oxide additions on the solubility of Ag₂O in KOH solutions was studied by Kovba and Balashova⁽¹⁵⁾ and Amlie and Ruetschi.⁽¹²⁾ Both pairs of workers concluded that zincate in the electrolyte has little or no effect on Ag₂O solubility. Kovba and Balashova used only one solution, 10 N KOH saturated with zinc hydroxide, and did not give quantitative results. Results reported by Amlie and Ruetschi are tabulated below:

| <u>Solution</u> | <u>[Ag(OH)₂]</u> |
|--|----------------------------------|
| 7.0 <u>N</u> KOH | 4.8 x 10 ⁻⁴ <u>N</u> |
| 7.0 <u>N</u> KOH & 1.9 <u>N</u> K ₂ Zn(OH) ₄ | 4.05 x 10 ⁻⁴ <u>N</u> |
| 5.04 <u>N</u> KOH | 4.7 x 10 ⁻⁴ <u>N</u> |
| 5.04 <u>N</u> KOH + 1.52 <u>N</u> K ₂ Zn(OH) ₄ | 4.3 x 10 ⁻⁴ <u>N</u> |

Effect of Temperature

As would be expected, increase of temperature increases the solubility of Ag₂O in KOH solutions. The data of Kovba and Balashova⁽¹⁵⁾ for 10 N KOH cover the widest temperature range. They observed the following:

| Temperature, C | $[\text{Ag}(\text{OH})_2^-]$ in 10 <u>N</u> KOH |
|----------------|---|
| 25 | 4.5, 6.0, 7.5×10^{-4} <u>N</u> |
| 50 | 7.0, 8.0, 9.0×10^{-4} <u>N</u> |
| 78 | 22.5, 24, 26×10^{-4} <u>N</u> |

The rather poor reproducibility of their data also is evident in this tabulation for triplicate experiments under supposedly identical conditions.

Dirkse⁽¹⁶⁾ reported results of Ag_2O solubility studies in 30, 40, and 45 percent KOH at 0, 10, and 25 C. Although Dirkse points out the values he reported "had a good deal of scatter", the relative solubilities at the three temperatures are probably better than the absolute values. His data are reproduced in Figure 3.

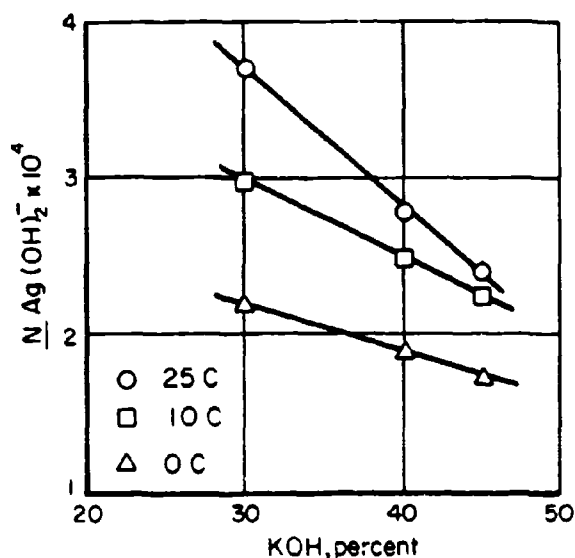


FIGURE 3. EFFECT OF TEMPERATURE ON THE SOLUBILITY OF Ag_2O IN KOH (from Dirkse)⁽¹⁶⁾

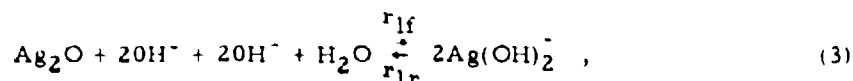
At the lowest temperatures at which silver-zinc batteries will operate, one might expect the solubility of Ag_2O to be about 1×10^{-4} N in the concentrated KOH electrolytes. Thermal cycling of cells could lead to repeated dissolution and reprecipitation of Ag_2O on the cathode, with resultant effects on the surface structure.

Equilibration and Decomposition of Solutions

The rate at which equilibrium is approached in studies of Ag_2O solubility has not been the specific objective of any of the investigators. From Table III, it can be seen that the various workers allowed equilibration times which ranged from 1 hour to

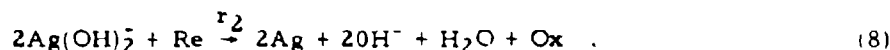
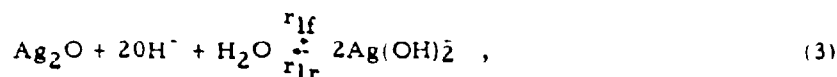
4 weeks. Usually, the time was selected on the basis of preliminary experiments to give constant values with time. The preliminary experiments, except for those of Dirkse⁽¹⁶⁾, were not reported in detail.

One way of explaining the variations found in solubility values for KOH stronger than 6 N is to postulate steady-state rather than equilibrium conditions. Thus, the reactions under equilibrium occurring are

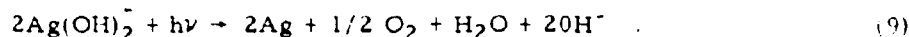


where r_{1f} and r_{2f} are the reaction rates (not rate constants) and $r_{1f} = r_{1r}$.

On the other hand, under steady-state conditions, various reactions could be responsible, but the most likely are



where $r_{1f} = r_{1r} + r_2$ and Re and Ox are the reduced and oxidized form of an impurity. An alternative to the reaction of Equation (8) is the photoinduced decomposition:



If it is assumed that the rate of attainment of equilibrium of Equation (3) is controlled by Equation (8) or (9), a study of the rates of attainment of equilibrium under various conditions should make it possible to determine what promotes the reaction of Equation (8) or if that of Equation (9) occurs. Dirkse⁽¹⁶⁾ has summarized results of several studies using this approach. He examined the effect of concentration of dissolved Ag_2O , KOH concentration, presence of solid ZnO, varying surface area of glass in contact with the solution, temperature, and the effect of light on rate of decomposition of Ag_2O in solution. As would be expected, the rate of decomposition increased with increasing $\text{Ag}(\text{OH})_2^-$ concentration and with increasing temperature. The rate of decomposition was greater in a transparent flask than in an opaque flask. Solid ZnO accelerated the decomposition, but an increase in the surface area of glass exposed to the solution had no effect on the rate. A minimum in decomposition rate was found at about 7 N KOH as KOH concentration was varied. Dirkse also found that certain organic materials, including methylcellulose, accelerated $\text{Ag}(\text{OH})_2^-$ decomposition when they were dissolved in the KOH solution.

The results of Dirkse's experiments do not lead to a definite conclusion about the mechanism of decomposition. However, it seems clear that at least two mechanisms must be postulated. One of these corresponds to the reduction of Equation (8) and is probably operative when an organic or solid ZnO is present, wherein the ZnO is suspected to be nonstoichiometric and to contain some Zn. The other mechanism corresponds to photoreduction of Equation (9) and occurs in the bulk of the solution - not on the glass surface. However, it is suspected that the presence of colloidal particles of silver or silver oxide can also affect the decomposition rate. Colloidal particles may provide the surface

where a photochemical reduction occurs or colloidal particles of Ag_2O or Ag may increase the analytical value, as Dirkse suggests, which would lead to solubility values which are too high.

Another reason for initially high solubility could be the greater solubility of small particles of silver oxide. The higher surface energy of small particles may cause supersaturation which subsequently disappears either by decomposition of the $\text{Ag}(\text{OH})_2^-$ or by precipitation.

II

THE PHASE RULE APPLIED TO BATTERY ELECTROLYTES

Statement of Phase Rule and Definitions

The phase rule was first obtained by J. Willard Gibbs in 1878. This rule, which will not be derived here, states that

$$F = C - P + 2 \quad , \quad (10)$$

where F = the number of degrees of freedom for the system, C = the number of components in the system, and P = the number of phases making up the system. In order to properly apply the phase rule, it is necessary to understand the meaning of each of these terms:

The number of degrees of freedom, F , of a system is the number of intensive variables which must be arbitrarily fixed to define the system. Another way of stating this is that the number of degrees of freedom is the number of intensive variables which can be independently varied without changing the number of phases in the system.

Commonly chosen degrees of freedom are the temperature, pressure, and concentration of various species in the system. The choice of such variables, however, is arbitrary and is usually made on the basis of convenience or clarity of presentation.

The number of components, C , of a system is the minimum number of pure chemical substances necessary to prepare arbitrary amounts of all the phases of the system.

It is important to note the term "pure chemical substances". For example, while a solution of NaCl in H_2O contains H^+ , Cl^- , Na^+ , and OH^- in varying degrees of hydration, there are only two pure chemical substances required to prepare the solution and the vapor in equilibrium with the solution.

A phase, P , is defined as the part of a system which is chemically and physically uniform throughout; it is bounded by a surface and is mechanically separable from the other parts (phases) of the system.

This uniformity is required only on a macroscopic level. Thus, ice is considered as one phase whether it is in one large block or in small chips, and a solution of alcohol in water is one phase even though it contains two chemical species when viewed at the molecular level.

Since the phase rule is derived from thermodynamic principles, it has the same utility and limitations as all other thermodynamic calculations. It is applicable only to equilibrium conditions, and tells nothing about the rate at which a system approaches equilibrium. An important application of the phase rule is that it tells the maximum number of phases which can be present under equilibrium conditions. Thus, if a system contains a greater number of phases, it cannot be at equilibrium. The condition $F = C - P + 2$ rigorously applies only in the absence of appreciable contributions to the

free energy by gravity, surface, or electrical effects. If such effects are appreciable, they must be considered just as in other thermodynamic calculations. (17) When such effects must be considered in systems to which the phase rule is applied, an additional degree of freedom is required for each additional type of energy which contributes to the free energy of the system.

Phase Rule Applied to Simple Systems

Consider, first, the application of the phase rule to a solution of KOH in H_2O . This system has two components which may be selected as KOH and H_2O . If the solution is unsaturated, there will be two phases; namely, vapor and liquid. According to the phase rule of Equation (10), this system has two degrees of freedom. These degrees of freedom may be taken as any two intensive variables, such as temperature, vapor pressure, KOH (or H_2O) concentration; or, any two other intensive properties may be chosen. The most commonly chosen pair of variables are temperature and KOH concentration. When the temperature and KOH concentration are fixed, all other intensive properties of the solution such as density, viscosity, and index of refraction are also fixed.

If the solution becomes saturated with KOH, there is, by definition of a saturated solution, solid KOH or one of its hydrates along with the liquid and vapor; thus, $P = 3$. The addition of this third phase removes one degree of freedom according to Equation (10), so that it is necessary to specify only one intensive variable to completely define the system. If this variable is chosen as temperature, one sees that the KOH concentration in the liquid phase is fixed. Thus, the concentration of a saturated KOH solution can be expressed as a function of temperature. The phase rule, however, gives no indication what the form of this function might be.

A third situation arises when a two-component system of a particular composition (known as the eutectic composition) is cooled. This system does not have a solid-liquid equilibrium over a range of temperatures as does a saturated solution. Instead, the system remains liquid until it reaches a certain temperature (known as the eutectic temperature) at which two pure-solid phases simultaneously appear. The system then contains four phases - two solids, a liquid, and a vapor - so that $F = 0$. Such a system with no degrees of freedom is known as an invariant system. The point on the phase diagram at which the above-described system becomes invariant is known as the eutectic point. For the system KOH- H_2O , the eutectic point is at a concentration of 30.9 percent KOH and at $-62.8^\circ C$. (18) The two solid phases of this system are ice and $KOH \cdot 4H_2O$.

A portion of a phase diagram for the system KOH- H_2O is shown in Figure 4, taken from Reference 19. In this diagram, which shows the above-mentioned eutectic, temperature and composition have been chosen as the intensive variables. This is the commonly chosen pair of intensive variables used in representing phase diagrams in the literature. Any other pair of intensive variables, however, could be used to describe the system. A system having two degrees of freedom lies within an area of a phase diagram. That is, it is necessary to specify two coordinates of the system to uniquely define the system. For instance, in this phase diagram it is necessary to state both the temperature and concentration of a solution containing KOH and water in equilibrium with its vapor to uniquely define all intensive variables. A system having one degree of

freedom lies on a line of such a phase diagram. As an example, it is necessary only to state the temperature of a solution containing KOH and water in equilibrium with its vapor and one pure solid. Finally, a system having no degrees of freedom is a point which is the intersection of two lines.

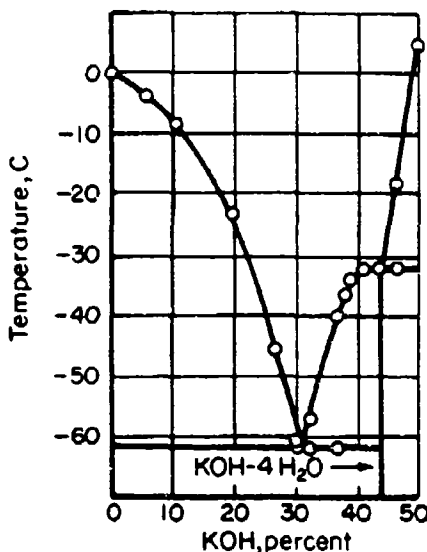


FIGURE 4. PORTION OF PHASE DIAGRAM FOR THE SYSTEM KOH-H₂O

(From Reference 19)

When a third component, such as K₂CO₃, is added to a solution of KOH, the situation becomes more complex. Now the system contains three components, KOH, K₂CO₃, and H₂O. When conditions are chosen so that the system is unsaturated in both KOH and K₂CO₃, there are two phases (liquid and vapor) containing the three components. This system has three degrees of freedom. These degrees of freedom may be taken as temperature and the concentrations of any two of the three components. (The third concentration is easily determined if concentrations are expressed as mole fractions or weight percent.) If this three-component system is saturated with K₂CO₃ at a given temperature there is still one degree of freedom. This is easily seen from the phase diagrams for this system at various temperatures found in Reference 20. The phase diagram for this system at 25 C is shown in Figure 5 using data from Reference 20. It is also seen that the solid phase present when the solution is saturated with K₂CO₃ but unsaturated with KOH is K₂CO₃ · $\frac{3}{2}$ H₂O except at the highest KOH concentrations. The composition of the stable solid phase in contact with a saturated solution is usually determined experimentally.

The addition of ZnO to a system containing KOH, K₂CO₃, and H₂O may complicate the system far beyond the addition of one more degree of freedom. Information on the chemistry of such solutions is very sparse so that it is only possible to speculate about the number of phases present. For instance, in a solution containing an excess of ZnO

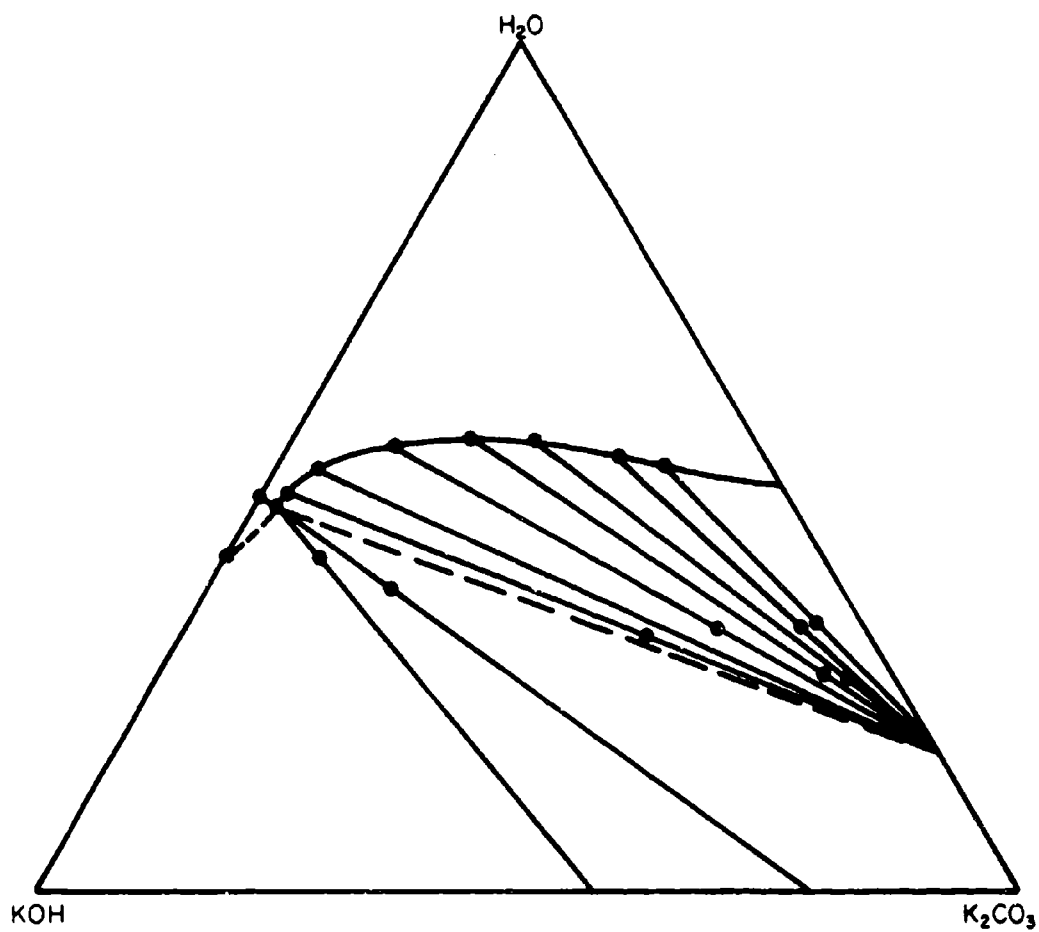
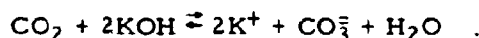


FIGURE 5. THE SYSTEM KOH-K₂CO₃-H₂O AT 25 C

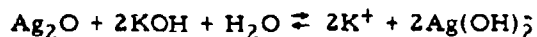
Data from Lang and Sukava⁽²⁰⁾

and an excess of K_2CO_3 the solid phases may react to form a more stable phase such as a zinc carbonate. If this happens, the various solution equilibria will shift and thus the solubilities of the various components are changed. If zinc carbonate is formed, the system will then contain five phases: vapor, solution, solid K_2CO_3 , solid ZnO and solid $ZnCO_3$. Since the system has four components: KOH , H_2O , K_2CO_3 , and ZnO , the phase rule allows only one degree of freedom which may be taken as temperature. Thus at a given temperature the system of four components and five phases is invariant. The phase rule does not tell us under what conditions this fifth phase will be formed or even if it will be formed at all. It does, however, tell us that (1) only a total of five phases can simultaneously occur over a range of temperatures, (2) that six phases can simultaneously occur at certain set temperatures, and (3) no more than six phases can ever occur in such a system. The rates at which various equilibria are approached may be quite slow so that times of the order of even a year may be required for the system to reach equilibrium. The same type of analysis is used when fifth component, Ag_2O , is added to the system except that number of components is increased to five and the number of solid phases must also be increased by one.

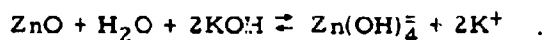
A five-component system probably approximates fairly well the actual electrolyte in a sealed $Ag-Zn$ cell after it has been cycled a number of times. The electrolyte, originally 40 weight percent KOH in H_2O , contains carbonate formed by reactions of CO_2 with the electrolyte according to



In addition, there is dissolved Ag_2O and ZnO from the electrodes which may dissolve according to the following reactions:



and



These are not the only equilibria that may be set up. Under certain circumstances there may also be equilibria involving such species as silver carbonate and zinc carbonate. Although the phase rule tells nothing about the nature of the equilibria involved or the presence or absence of various solid species, it does determine the maximum number of solid phases which are allowed. This will be discussed in the following section.

Zinc-Silver Oxide Battery Electrolyte

The alkaline electrolyte for the rechargeable zinc-silver oxide battery is generally added to the cell as a solution of Battery Grade potassium hydroxide adjusted to the desired concentration. It will generally contain a small amount of potassium carbonate; the concentration of this constituent will increase in the cell with time and use because of the oxidation of the separator materials, especially cellophane, and of any organic addition agents. For many applications, zinc oxide is dissolved in the electrolyte to decrease the open circuit stand losses and the hydrogen evolution from the zinc electrode. Finally, after use in the cell, the electrolyte will accumulate dissolved silver because of the presence of silver oxides in the positive electrodes. The battery electrolyte for the rechargeable zinc-silver oxide cell is thus a five-component system

consisting of water, potassium hydroxide, potassium carbonate, zinc oxide, and silver oxide. The rechargeable cell will generally be used under conditions producing both silver (I) oxide and silver (II) oxide. Fleischer has shown that with KOH electrolyte and the presence of the two oxides, the activity of silver in solution is fixed. (14) Therefore we may proceed with our study knowing that thinking in terms of dissolved silver and silver (I) oxide and excepting the conditions under which silver carbonate might be formed, the results for the solution phase will not be affected.

Five-component (or quinary) systems, even for the simplest case of only one stable solid phase per component, are usually complex especially with regard to their representation. A number of graphical methods have been established for special cases. (21) For a system of five components, the phase rule reduces to the equation, $F = 7 - P$. At equilibrium with a gas phase and a single solution phase, an invariant point at which the number of degrees of freedom is zero, would require the presence of five solid phases which might be $\text{KOH} \cdot 4\text{H}_2\text{O}$, $\text{K}_2\text{CO}_3 \cdot 3/2\text{H}_2\text{O}$, $\text{H}_2\text{O}_{(s)}$ (Ice), ZnO , and Ag_2O . If other phases, such as $\text{K}_2\text{CO}_3 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{OH})_2$, $2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2$ (hydrozincite), ZnCO_3 (smithsonite), or Ag_2CO_3 are capable of existence within certain ranges of temperatures and concentrations, additional invariant points will be expected. Such invariant points will be interconnected by univariant systems.

For the case of battery electrolyte for the silver-zinc oxide cells, the principal interest is confined to the five-component system with two solid phases, namely zinc oxide and silver (I) oxide. Under this condition, with five components and four phases, the system is trivariant. The solubility of silver oxide as a function of temperature can be fixed by selecting two concentration variables, such as the total potassium concentration and the ratio of total hydroxide concentration to carbonate concentration. The solubilities of the silver and zinc oxides in this four-phase system is determined at a given temperature by the appropriate equilibrium constants and thus are fixed for a given solution composition. However, if the quantity of KOH or K_2CO_3 in solution is varied, the solution equilibrium will be shifted so that the solubilities of Ag_2O and ZnO may be changed even though the number of phases in the system remains two solids plus liquid plus vapor.

The results of the experimental determinations of the solubility of silver (I) oxide at several ratios of hydroxide to carbonate will give an indication of the need for an extension of the study over the entire range of the quinary system. If it is found that there is little change in solubility, one would selectively complete the study to confirm the general trend. For example, the solubility of silver (I) oxide would be determined at the expected invariant systems and for selected univariant systems. These determinations could be supplemented at different total potassium concentrations and in the presence of silver (II) oxide. If the solubility of silver (I) oxide varies appreciably, it is clear that the solubility of this compound will have to be known for the various three-component and four-component systems.

III

REVIEW OF INFORMATION ON CONDUCTIVITIES AND FREEZING POINTS OF ELECTROLYTES USED IN SEALED SILVER-ZINC CELLS

Conductivity Literature

Electrolyte conductivity data are reported either as the specific conductance (or conductivity), K , or as the equivalent conductance, Ω . Equivalent conductance and specific conductance are related by

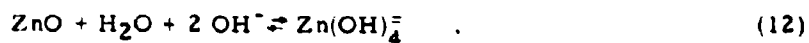
$$\Omega = \frac{1000}{C} K, \quad (11)$$

where C is the solution concentration in equivalents per liter. Specific conductance has units of $\text{ohm}^{-1}\text{cm}^{-1}$ and equivalent conductance has units of $\text{ohm}^{-1}\text{cm}^2 \text{equiv}^{-1}$. For a further discussion of the theory of electrolytic conduction the reader is directed to textbooks on basic physical chemistry such as that by Moore. (22)

Several studies of the conductivities of aqueous KOH electrolytes are available in the literature. Each study, however, covers only a limited number of temperatures and/or KOH concentrations. Also the various workers use different concentration units and different units to report their conductivity data so that comparison of data from the various sources requires that the data be converted from one set of units to another. For instance, Klochko and Godneva (23) measured the specific conductance of the KOH-H₂O system at 25, 75, 150, 175, and 200 C over the range 2.37 to 80.72 weight percent. Darken and Meir (24) report equivalent conductance over the range 0.06 to 10.61 normal at 25 C only. The conductivities of solutions of more limited KOH concentration ranges have been reported at extremely low temperatures (25). In this work the specific conductances of 30, 33, 35, and 40 weight percent KOH were measured over the range from -30 to -55 C where values of K from 0.01 to 0.07 $\text{ohm}^{-1}\text{cm}^{-1}$ were obtained. Also, Bodamer (26) reports the specific conductance of KOH solutions over the range of 35 to 46 weight percent at 10, 25, and 55 C. The same data are also reported in Reference 27. DeWane and Hamer (28) have tabulated equivalent conductance data from a number of sources at temperatures of 25, 30, 60, and 100 C.

Mixed electrolyte systems containing KOH, K₂CO₃, and H₂O, and KOH, ZnO, and H₂O have received limited attention. The specific conductivity of solutions containing KOH and K₂CO₃ were reported by Lake and Casey (29) over the range -54 to +20 C. These solutions were prepared so that the total K⁺ ion concentration was maintained the same as in 31 weight percent KOH. The specific conductance of these systems decreased with increasing carbonate concentration. The effect due to added ZnO on the specific conductance of KOH electrolytes is also reported. In one study (25) the effect of 2, 4, and 8 weight percent ZnO was studied over the range of -30 to -55 C in 25 to 35 weight percent KOH. Bodamer (26) had reported the effect of up to 8 percent ZnO in 35, 40, and 46 percent KOH at 10, 25, and 55 C. The addition of ZnO in all cases decreased the specific conductance from that of a pure KOH solution. This effect may be ascribed to a decrease in OH⁻ ion concentration produced by the hydrolysis of ZnO

according to the reaction



No conductivity data have been found in the literature for solutions containing KOH, K_2CO_3 and ZnO.

Table IV shows the specific conductance at 25 C for various KOH solutions over the range of interest for alkaline batteries. These data were taken from three different references and show good agreement between workers. A maximum in conductivity appears in the range of 30 weight percent KOH.

The specific conductance of aqueous KOH at 18 and 60 C was reported by Grube and Vogt(30). Their data, given in Table V, also show maxima with the maximum occurring at a lower concentration at the lower temperature. Comparison of the data in Tables IV and V shows that the specific conductance of KOH electrolytes at a given concentration increases with increasing temperature. Conductivity data for aqueous KOH are also reported in References 31 and 32.

TABLE IV. SPECIFIC CONDUCTIVITIES OF AQUEOUS KOH AT 25 C

| KOH, Wt % | K, ohm ⁻¹ cm ⁻¹ | Reference |
|-----------|---------------------------------------|-----------|
| 26.7 | 0.636 | 28(a) |
| 27.84 | 0.637 | 23 |
| 29.38 | 0.651 | 23 |
| 30.3 | 0.634 | 28(a) |
| 33.7 | 0.617 | 28(a) |
| 35.3 | 0.58 | 26 |
| 37.0 | 0.588 | 28(a) |
| 39.0 | 0.56 | 26 |
| 39.03 | 0.542 | 23 |
| 40.1 | 0.552 | 28(a) |
| 40.4 | 0.54 | 26 |
| 42.8 | 0.51 | 26 |
| 43.1 | 0.511 | 28(a) |
| 46.1 | 0.46 | 26 |
| 49.16 | 0.393 | 23 |

(a) Values calculated from equivalent conductance and concentration in equivalents per liter as given in reference.

TABLE V. SPECIFIC CONDUCTANCE OF AQUEOUS KOH
AT 18 AND 60 C. FROM REFERENCE (30)

| 18 C | | 60 C | |
|-------|---------------------------------------|-------|---------------------------------------|
| % KOH | K, ohm ⁻¹ cm ⁻¹ | % KOH | K, ohm ⁻¹ cm ⁻¹ |
| 24.9 | 0.55 | 27.8 | 1.078 |
| 29.6 | 0.58 | 30.3 | 1.091 |
| 33.7 | 0.52 | 32.4 | 1.091 |
| 38.1 | 0.48 | 38.1 | 0.007 |
| 42.3 | 0.41 | 42.3 | 0.992 |

Freezing Point Literature

The freezing points of aqueous KOH solutions may be obtained from phase diagrams of the KOH-H₂O system. Rollet and Cohen-Adad⁽¹⁸⁾ have determined a phase diagram for this system over the range -66 to 400 C for the complete concentration range from zero to 100 percent KOH. They report the eutectic point to be 30.9 weight percent KOH at -62.8 C. At lower KOH concentrations the solutions begin to freeze at higher temperatures. As such systems freeze, solid ice is formed and the remaining liquid becomes more concentrated in KOH. If the original solution has a KOH concentration greater than the eutectic composition, the solid which forms upon cooling will be a hydrate of KOH such as KOH·2H₂O or KOH·4H₂O. Which of these solid hydrates is first formed upon cooling is determined by the concentration of the starting solution and can be determined from the phase diagram for the system.

The effect of adding 2, 4, 6, and 8 weight percent ZnO to aqueous KOH solutions has been studied.⁽²⁵⁾ No solid species containing Zn were reported to be formed when these solutions are cooled. However, new hydrates of KOH such as KOH·2-1/2 H₂O, KOH·3H₂O and KOH·5H₂O were reported in addition to KOH·2H₂O and KOH·4H₂O. The eutectic composition of these solutions is reported to be 29.9 weight percent KOH for 2, 4, and 6 weight percent ZnO and 29.2 weight percent KOH for the solution containing 8 weight percent ZnO. The eutectic temperature was not specified but was below -60 C.

Phase diagrams for the system KOH-K₂CO₃-H₂O over the entire range of compositions are reported at temperatures from -60 to +25 C.⁽²⁰⁾ No compound formation between KOH and K₂CO₃ was reported over this temperature range. These data can be used to determine the liquid range of KOH-K₂CO₃ electrolytes at various temperatures as shown in Figure 6. The liquid region is bounded by the isothermal lines on the diagram. As the temperature decreases the region in which the electrolyte remains liquid becomes smaller.

As in the case of conductivity data, no data were found in the literature on the freezing points of aqueous solutions containing KOH, K₂CO₃, and ZnO.

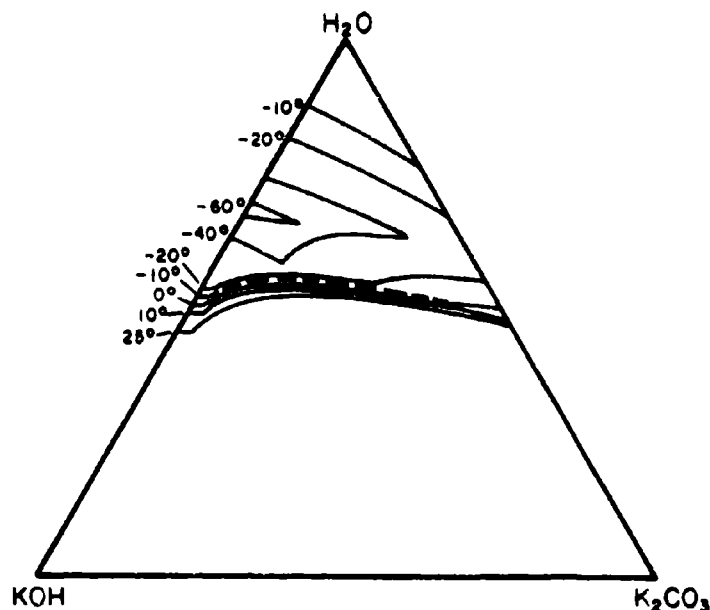


FIGURE 6. LIQUIDUS CURVES FOR THE SYSTEM KOH-K₂CO₃-H₂O
FROM 25 TO 60 C
(Reproduced from Reference 20.)

Other Physico-Chemical Properties

The density of aqueous KOH solutions was determined by Akerlof and Bender⁽³³⁾ at 10-degree intervals from 0 to 70 C for 0 to 50 weight percent KOH. The same authors later determined the mean molal activity coefficients of KOH over the same temperature and concentration range.⁽³⁴⁾

The apparent hydroxide ion transference number for aqueous KOH at 20 C is reported to be 0.78 over the concentration range 3 to 12 molal.⁽³⁵⁾ This value decreased to 0.74 at 1 and 17 molal. The apparent hydroxide ion transference number remains constant while the conductivity goes through a maximum in the same concentration range. The constancy of the transference number suggests that the mobile species and their relative mobilities remain the same over this concentration range while the decrease in conductivity at higher concentrations suggests a decrease in the actual mobility values. Such a decrease in mobility is probably related to increased viscosity and changes in the clathrate structure of the water.

Physical properties of aqueous KOH electrolytes have been summarized by Cooper and Fleischer⁽³⁶⁾ and by Milner and Thomas⁽³⁷⁾.

IV

EXPERIMENTAL PROCEDURES

In the first portion of the experimental work, the study of silver oxide solubility was directed toward determining the equilibrium concentration of $\text{Ag}(\text{OH})_2$ in KOH solutions saturated with solid Ag_2O . Measurements were made at 0 C and 25 C with potassium hydroxide concentrations from 2 N to 12 N.

Certified reagent-grade potassium hydroxide was purchased as a 45 weight percent solution in a polyethylene package. About 3.5 liters of solution were transferred directly to a polyethylene bottle equipped with two platinum electrodes each having an area of 4 cm². Electrolysis* to remove inorganic and organic impurities was carried out at about 0.5 ampere for 60 to 70 hours with an argon atmosphere to displace the hydrogen and oxygen evolved.

For dilution of the concentrated KOH solution, double distilled water was used. Bottled distilled water was introduced into an all Pyrex system where it was first filtered through activated charcoal (Barnaby-Cheney Type 5A) into a still pot containing alkaline permanganate solution. The vapor was passed through an insulated vertical column about 1 meter long and thence to a condenser and a collection flask.

Silver oxide purchased from Industrial Chemicals Division, Allied Chemical Corporation, was purified by boiling in distilled water for several hours followed by decanting and drying. The silver analysis was increased by this procedure from 92.25 to 93.11 percent by weight of silver. The theoretical value is 93.10 percent.

A glove bag with argon atmosphere was used for sample preparation. Small mouth, screw-top, 250-ml Teflon bottles were used for the samples. The screw caps of the bottles had Teflon liners so that the solution was only in contact with Teflon. About 50 mg of the purified Ag_2O and two, 3 x 1/4-inch Teflon tumbling rods were placed in each bottle. The required quantity of 45 weight percent KOH and distilled water was measured into each bottle using a Pyrex graduated cylinder (the only contact the solution had with glass until the analysis step). About 125 ml of solution was used for each sample of different KOH concentrations. The bottles were closed with an argon atmosphere inside.

The sample bottles were then transferred to an atmosphere chamber and placed in a specially constructed bottle-turning apparatus and immersed in a constant-temperature bath. The atmosphere in the chamber was "zero grade" air containing less than 1.5 ppm total hydrocarbons and about 0.5 ppm carbon dioxide. For experiments at room temperature, water was used in the constant-temperature bath; for low temperature, a calcium-chloride brine was used. The bottle-turning apparatus is described in Appendix I.

After an equilibration time of at least 7 days during which the chamber remained dark, the samples were removed and filtered to remove undissolved Ag_2O . The contents of a bottle was placed in a Seitz silver-plated, steel pressure filter. A porous Teflon pad with 1- to 5-micron-diameter pores served as the filter medium. The initial

*After this work was done, it was shown ⁽⁴¹⁾ that such pre-electrolysis can contaminate the electrolyte with dissolved platinum. For this reason, pre-electrolysis was omitted in later work.

portion of filtrate from each sample was discarded. This provided the washing action needed on the filter to allow it to be used for several samples in succession. Application of purified air at 5 to 15 psi allowed pressure filtration to be completed in about 5 minutes. Filtered solutions were brought out of the chamber in a beaker covered with dark paper.

Aliquots of the filtrate were removed for analysis as soon as possible. The analytical procedures are also detailed in Appendix I.

Part II. Silver Oxide Solubilities and Physical Properties of Battery Electrolytes

The second part of the solubility studies was primarily concerned with the solubility of silver in the presence of CO_3^{2-} and ZnO . Five solutions were prepared. One was nearly carbonate-free while the other four were prepared containing known amounts of K_2CO_3 up to saturation, keeping the potassium ion concentration constant. The five solutions were prepared using the following amounts of material:

Solution I: 382.5 ml of 45% KOH diluted to 450 ml and added to 60 grams ZnO and 0.125 g Ag_2O .

Solution II: 380.0 ml of 45% KOH diluted to 450 ml and added to 60 grams ZnO , 0.125 g Ag_2O and 2.25 g K_2CO_3 .

Solution III: 372.5 ml of 45% KOH diluted to 450 ml and added to 60 grams ZnO , 1.25 g Ag_2O and 9.0 g K_2CO_3 .

Solution IV: 354.5 ml of 45% KOH diluted to 450 ml and added to 60 grams ZnO , 0.125 g Ag_2O and 22.5 g K_2CO_3 .

Solution V: 336.5 ml of 45% KOH diluted to 450 ml and added to 60 grams ZnO , 0.125 g Ag_2O and 54.0 g K_2CO_3 .

Duplicate samples of these five solutions were made. They were identified as bottle 1 and bottle 2.

Reagent-grade chemicals and KOH were used for all tests. Teflon bottles (500 ml) were used as containers for the solutions. The bottles were leached with a 1:1 ratio of HNO_3 and H_2SO_4 for at least 24 hours after which they were thoroughly rinsed with deionized water and finally with double distilled water.

The solid materials were weighed and placed in the appropriate bottles. Sufficient solution was made for both samples of a solution. This was divided and also added to the appropriate bottles. Double distilled water was used to dilute the KOH to the proper concentration.

Just prior to insertion into the bottle turning apparatus, each bottle was shaken vigorously to disperse the solid material throughout the solution. This action was repeated at various times during the equilibration periods.

The solutions were equilibrated in the temperature sequence -25 C, 0 C, 25 C, 40 C, and -25 C. The scheduled equilibration period at each temperature was 7 days. However because of temperature control and experimental problems, the equilibration period varied from 8 days to 30 days at the particular temperatures. A description of the bottle-turning and constant-temperature apparatus can be found in Appendix I.

After the equilibration period, a 50-ml aliquot was removed from one of the two sample bottles of each particular solution. At -25 C the aliquots were taken from bottle 1 of each of the five solutions; at 0 C, from bottle 2; at 25 C, from bottle 1; at 40 C, from bottle 2; and at -25 C (second time), from bottle 2. Immediately after each aliquot was removed it was filtered to remove any undissolved solid particles. Filtering was done using a type L-6 Seitz silver-plated steel pressure filter. A porous Teflon pad with 5 to 10 μ diameter pores served as the filter membrane. A nitrogen pressure of 1-5 psi was used during filtration. The aliquots were filtered into thoroughly cleaned polyethylene bottles for storage.

After each filtering, the filter and its membrane was disassembled and thoroughly washed with deionized water to remove any residue. The filter was dried and nitrogen passed through it before the next aliquot was filtered. All filtering occurred at room temperature.

Immediately after filtering, the filtered sample was placed in an environmental chamber set at the same temperature as which the aliquot had been equilibrated. While in the chamber, samples were taken for density measurements and the conductivity of the solution was measured. The density was determined from the weight of a known volume of solution. The conductivity was determined by a Wayne Kerr Universal Bridge B221A using a conductivity loop cell C321. An 1.0 N KCl solution at 25 C was used as a standard.

After the conductivity had been determined and a sample had been obtained for the density measurements, the solutions were removed from the environmental chamber for chemical analysis. The analytical procedures are described in Appendix I. All chemical analysis was conducted at room temperature.

Two additional experiments were performed to consider the rate of dissolution and particle size of solid Ag_2O on solubility. The first consisted of preparing a solution the same as the previously described solution IV. That is 354.5 ml of 45 percent KOH diluted to 450 ml and added to 60 grams ZnO , 0.125 grams Ag_2O and 22.5 grams K_2CO_3 . This solution was prepared in the same manner as previously described solutions except that only one 450-ml sample was made. The solution was placed in the temperature bath, which was maintained at 25 C. A 50-ml aliquot of the sample was removed after 0.2 hours, 2.0 hours, 20.0 hours, and 200.0 hours. These aliquots were filtered using the same equipment and procedures described previously in this part. Likewise the same analytical procedures were followed.

After the chemical analysis had been concluded, the freezing points of each of the five solutions was determined. A 50-ml aliquot was taken from bottle 1 of each solution and filtered as previously mentioned. Approximately 35 ml of each solution was placed in a 50-ml beaker and a thermocouple was suspended in the liquid of the beaker. The beakers were placed in a Tenney Model 14 environmental chamber capable of -100 F.

Once the chamber and solutions had been prepared, the chamber was set for -100 F and remained at that setting until the solution froze. Cooling curves for each of the solutions were recorded by connecting the thermocouples to a multichannel recorder.

RESULTS AND DISCUSSION

Part I. Silver Oxide Solubility in Potassium Hydroxide

The experimental work, as described in Chapter IV, was performed in two separate parts. In the first part, the solubility of Ag_2O as a function of KOH concentration was determined at 0 and 25 C. These data are shown in Table VI. The first measurements of Ag_2O solubility were made at 25 C. The reproducibility of these measurements was quite poor so that the confidence to be placed in them is questionable.

Less experimental difficulty was encountered in the measurements made on solutions equilibrated at 0 C so that these data are believed to be valid. These data show a maximum of Ag_2O solubility at about 6 N KOH as has been reported for measurements at 25 C by other workers.

TABLE VI. SOLUBILITY OF Ag_2O IN KOH
AT 0 AND 25 C

| 0 C | | 25 C | |
|--------|---------------------------|--------|---------------------------|
| KOH, N | Ag_2O , N | KOH, N | Ag_2O , N |
| 2.07 | 1.08×10^{-4} | 4.27 | 1.10×10^{-4} |
| 4.17 | 1.20 | 4.28 | 1.30 |
| 6.24 | 1.65 | 4.32 | 3.45 |
| 8.17 | 1.47 | 4.43 | 4.20 |
| 10.07 | 1.32 | 4.42 | 4.85 |
| 11.95 | 1.24 | 8.71 | 3.70 |
| 12.10 | 1.13 | 11.33 | 3.20 |
| | | 12.08 | 3.93 |

Part II. Silver Oxide Solubilities and Physical Properties of Battery Electrolytes

The electrolyte systems used in this work contained KOH and K_2CO_3 in varying amounts such that the total potassium ion concentration was that of a 40 weight percent KOH solution. All solutions were saturated with ZnO and Ag_2O . Under these conditions the solubility of Ag_2O was found to be considerably less than in pure 40 percent KOH. The solubility of Ag_2O in pure 40 percent KOH at 25 C was determined towards the end of this part of the work to be $1.7 \pm 0.3 \times 10^{-4}$ N, whereas the solubility of Ag_2O in ZnO-saturated 40 percent KOH was 5.5×10^{-6} N in Solution I of Table VII. This solubility depression by ZnO is in contrast to the negligible effect of ZnO on the solubility of Ag_2O reported by Kovba and Balashova⁽¹⁵⁾, and by Dirkse⁽¹⁶⁾. The complete analysis of the five solutions at each temperature is given in Table VII. The

TABLE VII. ANALYSIS OF KOH, K_2CO_3 , ZnO, AND Ag_2O IN ELECTROLYTES

| | -25 C | 0 C | 25 C | 40 C | -25 C |
|---------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| <u>Solution I</u> | | | | | |
| KOH, \underline{N} | 7.36 | 7.35 | 7.41 | 7.38 | 7.33 |
| K_2CO_3 , g/l | 0.39 | | | | |
| ZnO, g/l | 95.4 | 99.9 | 99.7 | 98.5 | 99.5 |
| Ag_2O , \underline{N} | | 4.1×10^{-6} | 5.5×10^{-6} | 3.9×10^{-6} | 3.5×10^{-6} |
| <u>Solution II</u> | | | | | |
| KOH, \underline{N} | | 7.31 | 7.39 | 7.38 | 7.31 |
| K_2CO_3 , g/l | | 2.74 | 2.14 | 0.51 | |
| ZnO, g/l | | 97.8 | 98.7 | 97.4 | 99.3 |
| Ag_2O , \underline{N} | | 3.1×10^{-6} | 2.9×10^{-6} | 1.2×10^{-6} | 1.2×10^{-6} |
| <u>Solution III</u> | | | | | |
| KOH, \underline{N} | | 7.43 | 7.46 | 7.51 | 7.45 |
| K_2CO_3 , g/l | | 1.54 | 0.75 | 0.37 | |
| ZnO, g/l | | 94.2 | 92.7 | 94.2 | 96.0 |
| Ag_2O , \underline{N} | | 2.0×10^{-6} | 1.6×10^{-6} | 1.4×10^{-6} | 2.0×10^{-6} |
| <u>Solution IV</u> | | | | | |
| KOH, \underline{N} | 7.26 | 7.40 | 7.41 | 7.43 | 7.31 |
| K_2CO_3 , g/l | 4.87 | 5.72 | 8.42 | 6.68 | 7.33 |
| ZnO, g/l | 83.6 | 84.9 | 84.0 | 84.5 | 85.6 |
| Ag_2O , \underline{N} | 3.5×10^{-6} | 2.7×10^{-6} | 1.6×10^{-6} | 1.4×10^{-6} | 1.2×10^{-6} |
| <u>Solution V</u> | | | | | |
| KOH, \underline{N} | 7.02 | 7.07 | 7.10 | 7.11 | 7.12 |
| K_2CO_3 , g/l | 67.4 | 68.3 | 66.8 | 65.9 | 62.7 |
| ZnO, g/l | 71.5 | 76.2 | 75.0 | 77.2 | 77.5 |
| Ag_2O , \underline{N} | 3.9×10^{-6} | 2.9×10^{-6} | 1.4×10^{-6} | | 2.0×10^{-6} |

silver analysis is omitted in two locations in this table because in these two cases some solid particles of Ag_2O passed through the Teflon filter. This caused the experimentally determined silver concentration to be greater by about an order of magnitude. These particles remained suspended in solution even after repeated filtration. The experimental error in determining the normality of the dissolved Ag_2O is estimated to be about $\pm 1.0 \times 10^{-6} \text{ N}$.

The solubility of Ag_2O in pure 40 percent KOH (about 10 N) determined in the present work is lower by almost a factor of 2 than that determined by other workers shown in Figure 1. This further discrepancy in the solubility of Ag_2O in concentrated KOH solutions serves to emphasize the uncertainty with which the literature on this subject must be viewed.

The analyses of Solutions II and III in the first -25 C column of Table VII contained obviously gross experimental errors. After all the analytical work had been completed, fresh samples of these two solutions were prepared and equilibrated for 4 days before portions were withdrawn for analysis. The results of these analyses are:

| <u>Solution</u> | <u>II</u> | <u>III</u> |
|-------------------------------|----------------------|----------------------|
| KOH, N | 7.90 | 7.81 |
| K_2CO_3 , g/l | 3.18 | 2.21 |
| ZnO, g/l | 77.9 | 81.9 |
| Ag_2O , N | 9.2×10^{-6} | 2.9×10^{-6} |

The KOH concentration is greater and the ZnO concentration is lower in these two solutions which were allowed to equilibrate for a longer period of time. This suggests that the ZnO had not reached its steady state value in a period of 4 days. The rate at which an equilibrium, or at least steady state, condition is reached is considered further below.

The variation of the Ag_2O solubility with temperature in the solutions studied appears to be independent of temperature within the estimated experimental error, $\pm 1 \times 10^{-6} \text{ N}$. As the carbonate concentration in the solutions increases, there is a slight decrease in Ag_2O solubility. This is seen most clearly between Solutions I and II, the former of which was carbonate-free.

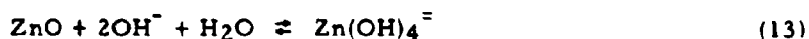
The solubility of ZnO is essentially independent of temperature within the experimental error of analysis at any carbonate level. This is in concurrence with data reported by Dirkse in pure KOH(38). The ZnO solubility also decreases with increasing carbonate concentration. The decrease in solubility of Ag_2O and ZnO with increasing carbonate concentration suggests the formation of insoluble Ag_2CO_3 and ZnCO_3 . The phase rule provides a basis for determining the maximum number of phases which can be present simultaneously. If the system contains five components, the phase rule states that the number of degrees of freedom, F, of the system is given by

$$F = 7 - P.$$

If an arbitrary temperature is selected for the system, there will be one less degree of freedom. Therefore, six phases are required to make the system invariant. This is the maximum number of phases which can be present simultaneously in the system. It is important to note, however, that the actual number may be less than this maximum number and is determined by the chemistry of the system. The system being considered in this discussion are known to contain at least four phases; namely, vapor, solution, solid ZnO, and solid Ag₂O. According to the phase rule, two more solid phases may also be present. If the solution is saturated with K₂CO₃, only one more solid phase is permitted.

The data of Table VII shows that solubility of ZnO decreases with increasing amounts of K₂CO₃ in the system which suggests the formation of insoluble ZnCO₃. The effect of ZnCO₃ in a silver-zinc battery with regard to the charge-discharge characteristics of the battery should be a subject of further investigation.

The dissolution of ZnO in KOH according to



consumes two moles of KOH for every mole of ZnO dissolved. On the basis of this stoichiometry, the values of KOH normalities shown in Table VII must be increased by the amounts shown in Table VIII to arrive at the original KOH concentrations which are also shown in Table VIII.

TABLE VIII. CALCULATED KOH CONSUMED DURING DISSOLUTION OF ZnO

| | -25 C | 0 C | 25 C | 40 C | -25 C |
|---------------------|-------------|------|------|------|-------|
| | Moles/Liter | | | | |
| <u>Solution I</u> | | | | | |
| KOH Consumed | 2.34 | 2.46 | 2.45 | 2.42 | 2.44 |
| Original KOH | 9.70 | 9.81 | 9.86 | 9.80 | 9.70 |
| <u>Solution II</u> | | | | | |
| KOH Consumed | | 2.41 | 2.43 | 2.39 | 2.44 |
| Original KOH | | 9.72 | 9.82 | 9.77 | 9.75 |
| <u>Solution III</u> | | | | | |
| KOH Consumed | | 2.32 | 2.28 | 2.32 | 2.36 |
| Original KOH | | 9.75 | 9.74 | 9.83 | 9.81 |
| <u>Solution IV</u> | | | | | |
| KOH Consumed | 2.06 | 2.09 | 2.07 | 2.08 | 2.10 |
| Original KOH | 9.32 | 9.49 | 9.48 | 9.51 | 9.41 |
| <u>Solution V</u> | | | | | |
| KOH Consumed | 1.76 | 1.88 | 1.85 | 1.90 | 1.91 |
| Original KOH | 8.78 | 8.95 | 8.95 | 9.01 | 9.03 |

Table VIII shows that the original KOH concentration decreases as one goes from Solution I to Solution V. This is because of the increasing K_2CO_3 concentration with increasing solution number. The original KOH concentrations of Solution I which contains no K_2CO_3 are between 39 and 40 weight percent KOH. The effect of the density change upon ZnO dissolution on these concentrations will be discussed below. The quantity of KOH consumed during the dissolution of Ag_2O according to



is negligible for these calculations.

The densities of these five solutions were measured at each temperature. These values are given in Table IX. All values are about 6 percent greater than the value of 1.3942 interpolated from the data of Ackerloff and Bender⁽³³⁾ for 40 weight percent KOH at 25 C. These data shows that the dissolution of ZnO in 40 percent KOH causes an increase in the solution volume. Consider one liter the ZnO-saturated 40 percent KOH solution at 25 C. According to Table IX, this solution weighs 1467.9 g, and from

Table VII, it contains 99.7-g ZnO. Thus the weight of the 40 percent KOH solution is 1368.2 g. One liter of pure 40 percent KOH, however, weighs 1394.2 g. Thus one liter of the ZnO-saturated 40 percent KOH required $1368.2/1394.2 = 0.981$ liter of pure 40 percent KOH. The density of solid ZnO is 5.606⁽³⁹⁾ so that 99.7 of ZnO occupies 17.8 ml. It is thus seen that the increase in solution volume upon dissolution of ZnO in 40 percent KOH can be accounted for by considering the volumes of 40 percent KOH and solid ZnO to be additives. Also the data show that the original KOH concentrations as determined above by adding experimental KOH and ZnO concentrations must be increased by the ratio 1394.2/1368.2 at 25 C. Thus, the corrected original KOH concentration for the ZnO-saturated solution at 25 C is 40.1 percent.

TABLE IX. MEASURED DENSITIES OF KOH, K₂CO₃, ZnO, AND Ag₂O ELECTROLYTES

| | -25 C | 0 C | 25 C | 40 C | -25 C |
|--------------|--------|--------|--------|--------|--------|
| Solution I | 1.4940 | 1.4836 | 1.4679 | 1.4646 | 1.5071 |
| Solution II | 1.4932 | 1.4850 | 1.4710 | 1.4595 | 1.4935 |
| Solution III | 1.4889 | 1.4904 | 1.4644 | 1.4649 | 1.4897 |
| Solution IV | 1.4785 | 1.4733 | 1.4592 | 1.4571 | 1.4770 |
| Solution V | 1.4866 | 1.4884 | 1.4705 | 1.4634 | 1.4963 |

Electrolyte Conductivities. The specific conductances, K, of each of the five solutions is given in Table X. The conductance of the solutions increases with increasing temperature and decreases with increasing carbonate concentration. Since the hydroxide concentration decreases with increasing carbonate concentration, the decrease in conductivity is due to the lower mobility of carbonate ions.

An average of two measurements on 10 N Ag₂O saturated KOH gave a conductivity of 0.529 ohm⁻¹cm⁻¹. The literature value of the conductivity for this concentration of KOH shown in Table IV is 0.55. This small variation can be ascribed to slight variations in experimental procedure equally as well as to the effect of dissolved Ag₂O.

TABLE X. CONDUCTIVITIES OF ELECTROLYTES
CONTAINING KOH, K_2CO_3 , ZnO,
AND Ag_2O

| | -25 C | 0 C | 25 C | 40 C | -25 C |
|--------------|---|-------|-------|-------|--------|
| Solution I | 0.0665 ohm ⁻¹ cm ⁻¹ | 0.177 | 0.424 | 0.514 | 0.0761 |
| Solution II | 0.0662 | 0.180 | 0.410 | 0.499 | 0.0747 |
| Solution III | 0.0693 | 0.182 | 0.405 | 0.516 | 0.0733 |
| Solution IV | 0.0645 | 0.185 | 0.389 | 0.502 | 0.0710 |
| Solution V | 0.0755 | 0.166 | 0.364 | 0.482 | 0.0721 |

Effect of Time on Solution Composition. The rate at which an equilibrium, or at least steady state, condition is reached in solutions containing KOH, Ag_2O , ZnO, and K_2CO_3 has not been thoroughly studied in the literature although it is suggested that this rate may be relatively slow. Two experiments were performed to determine if, indeed, time effects were important in such studies. The first experiment was a repetition of the solution analyses at -25 C after the solutions had been equilibrated at the various higher temperatures. This second set of measurements was made about 8 weeks after the first set of measurements at -25 C. The data in Table VII show that in all experiments, the quantity of dissolved ZnO is greater in the second set of measurements.

The second experiment consisted of withdrawing and analyzing samples of a solution containing KOH, Ag_2O , ZnO, and K_2CO_3 after 0.2, 2.0, 22, 200 hours. This solution contained the same quantities of these components as did Solution IV of Table VII. The results of the analyses after various equilibration times are given in Table XII. Conductivity measurements at 25 C are also given.

TABLE XI. SOLUTION COMPOSITION AND CONDUCTIVITY
AS A FUNCTION OF TIME

| | 0.2 Hr | 2 Hr | 22 Hr | 200 Hr |
|---------------------------------------|--------------------------|----------------------|----------------------|----------------------|
| KOH, <u>N</u> | 7.37 | 7.46 | 7.43 | 7.51 |
| K_2CO_3 , g/l | 27.2 | 17.7 | 13.3 | 8.15 |
| ZnO, g/l | 72.8 | 82.2 | 84.6 | 85.8 |
| Ag_2O , <u>N</u> | 3.0×10^{-5} (a) | 1.8×10^{-6} | 1.8×10^{-6} | 5.5×10^{-6} |
| K, ohm ⁻¹ cm ⁻¹ | 0.413 | 0.403 | 0.398 | 0.358 |

(a) Suspended silver particles in solution caused high value.

The data of Table XI show an increase in ZnO concentration and a decrease in K_2CO_3 concentration with time. The values of these concentrations after 200 hours are very similar to the values for Solution IV at 25 C shown in Table VII thereby indicating steady state at 200 hours. The conductivity after 200 hours is also similar to that of Solution IV at 25 C shown in Table X.

Freezing Points. Accurate freezing points of the solutions could not be obtained by measuring the solution temperature as a function of time while the solution was cooled in a Tenney refrigeration chamber. Measurements were attempted using both large (35 ml) and small (2 ml) volumes of electrolyte samples. Supercooling was generally observed when the large volumes of electrolyte were used. A representative curve of this type is shown in Figure 7.

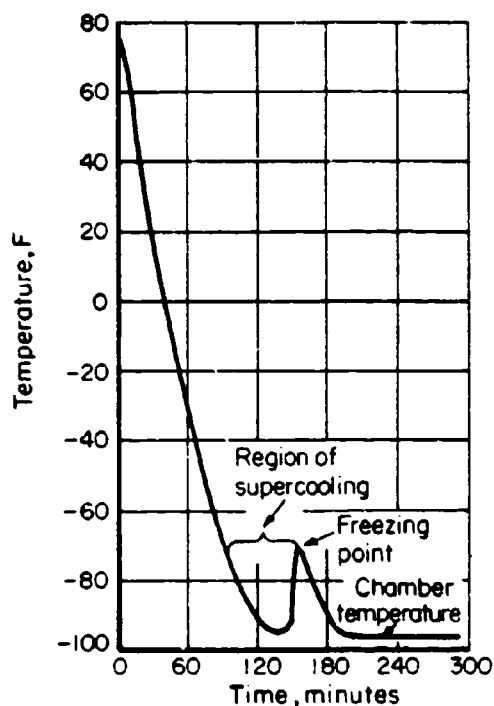


FIGURE 7. COOLING CURVE FOR SOLUTION I

While this curve does show a point at which the solution became frozen, this point is thought to be lower than the true freezing point of the solution because of the thermal inertia associated with systems having large heat capacities. The freezing points measured from cooling curves of the five solutions are given in Table XII. No freezing point was obtained for Solution V since it remained unsolidified at -96 F which was the lowest temperature attainable with the refrigeration system used.

TABLE XII. FREEZING POINTS OF ELECTROLYTE SOLUTIONS DETERMINED FROM COOLING CURVES

| Solution | Freezing Point |
|----------|----------------|
| I | -69 F = -51 C |
| II | -78 F = -61 C |
| III | -78 F = 61 C |
| IV | -90 F = 68 C |
| V | --- |

Warming curves were also obtained on these solutions to determine melting points which would not show the effect of supercooling. These curves showed a change of slope which was taken to be the melting point. The melting points are given in Table XIII.

TABLE XIII. MELTING POINTS OF ELECTROLYTE SOLUTIONS DETERMINED FROM WARMING CURVES

| Solution | Melting Point |
|----------|---------------|
| I | -21 F = -29 C |
| II | -25 F = -32 C |
| III | -37 F = -38 C |
| IV | -33 F = -36 C |
| V | -30 F = -34 C |

These values are thought to be closer to the true freezing points than the values given in Table XII because superheating is less apt to occur than supercooling. There is no way to predict the freezing or melting points of these four-component systems without a knowledge of the system's phase diagram. For comparison the freezing point of pure 40 percent KOH obtained by interpolating data of Rollet and Cohen-Adad⁽¹⁸⁾ is -37.1 C.

No breaks in either cooling or warming curves were observed when 2-ml electrolyte samples were used even though the solutions were observed to freeze and melt.

VI

CONCLUSIONS

The results of this study show that the properties of electrolytes found in silver-zinc batteries are quite different than those of pure 40 percent KOH. For example, when 40 percent KOH is saturated with ZnO

- (1) The solubility of Ag_2O is about 100 times less than in pure 40 percent KOH.
- (2) The conductivity is decreased by about 20 percent at 25 C.
- (3) Supercooling and thermal hysteresis are pronounced in battery electrolytes. Some indication was obtained that zinc oxide saturations raised the freezing point of 40 percent KOH.

The addition of potassium carbonate to zinc oxide-saturated KOH solutions decreases the solubility of ZnO in these solutions. Also the volume of ZnO-saturated 40 percent KOH solutions can be accounted for by considering the volumes of 40 percent KOH and solid ZnO to be additive.

These and other results are important when one wishes to consider the effect of the electrolyte on the operation of silver-zinc batteries. For instance, the internal resistance of a battery increases with increasing carbonate concentration in the electrolyte. This increased resistance may cause the voltage of a battery to drop below a tolerable value, thereby indicating failure of the battery. A knowledge of the magnitude of this effect will allow the voltage drop due to increased internal resistance to be compensated for when designing a battery.

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APPENDIX

APPARATUS AND PROCEDURES FOR SILVER OXIDE SOLUBILITY DETERMINATION

Apparatus

Bottle-Turning Apparatus. A photograph of this apparatus is presented in Figure 8. The spindles with the attached clamps are held in the mechanism with a spring-loaded rod riding in a groove in the spindle. This arrangement allows easy emplacement and removal of the bottles in a limited space. The entire apparatus, without bottles, weighs about 25 pounds and can be rested on the edge of the constant-temperature bath and adjusted to the desired angle by means of brackets which can be seen in the figure. The apparatus is powered by a 1/20 hp continuous duty motor which rotates the bottles six revolutions per minute.

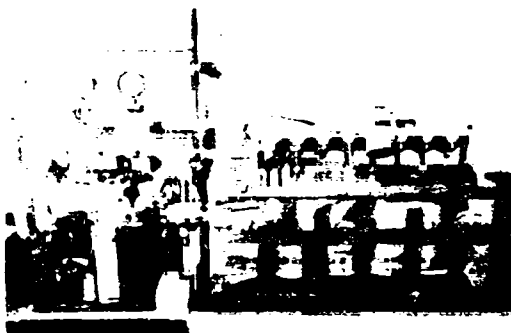
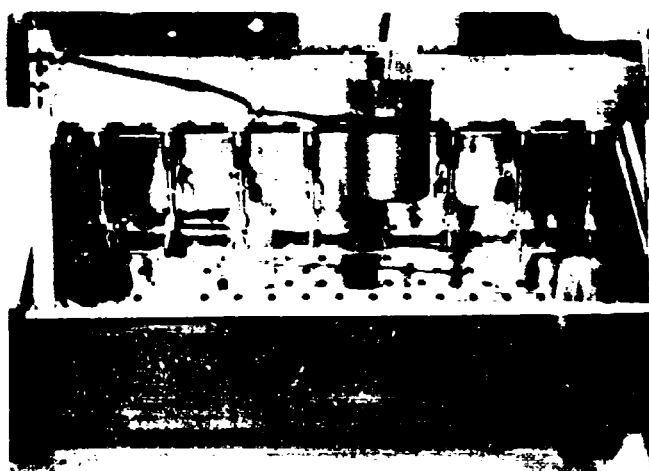


FIGURE 8. CONSTANT-TEMPERATURE APPARATUS

Constant-Temperature Apparatus. Figure 9 shows the bottle-turning apparatus, constant temperature bath, and compressor unit used in Part II of the solubility studies. Cooling coils were placed in the bottom of the temperature bath to obtain the low temperatures. Temperature control was obtained by inserting a small heating wire also in the bottom of the bath. The cooling system was permitted to operate continuously and heat was introduced to the system to attain the desired temperature. A 50 percent solution of glycol was used in the temperature bath for all temperatures. A copper tube with small holes drilled in it, through which air was bubbled, was placed in the bottom of the bath under the heating and cooling coils. This provided the agitation needed to maintain a constant temperature throughout the bath. At the lower temperatures, the temperature of the bath was controllable to ± 1.0 F.



a. Bottle-Turning Apparatus, Bottom View Showing Spindle Sockets and Support Brackets at Each End



b. Bottle Turning Apparatus in Constant-Temperature Bath (Without Water), Clamps and Bottles Mounted in Some Spindle Sockets

FIGURE 9. SIXTEEN-SPINDLE BOTTLE-TURNING APPARATUS

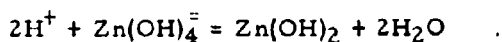
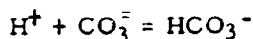
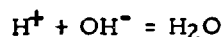
Analytical Procedures

The procedure for chemical analysis of the solutions varied somewhat depending on whether zincate and carbonate were added or not. Solutions containing no carbonate or zincate were analyzed for KOH concentration by titration with standard 1.0 N HNO_3 using a pH meter as the indicator. When the KOH solutions contained dissolved K_2CO_3 and ZnO the procedure given below was used. The procedure was checked by first analyzing a solution containing known weights of KOH and ZnO. Further preliminary experiments showed that the presence of ZnO did not interfere with the subsequent determination of Ag_2O and vice-versa.

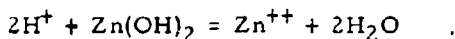
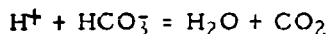
KOH, K_2CO_3 , and ZnO. A 5.00 ml aliquot of the solution was pipetted into a 250 ml beaker containing 50 ml deionized water. This solution was titrated with standard nitric acid to pH 8 using two drops of phenolphthalein indicator. The color change is from pink to colorless. Three drops of methyl orange indicator were added and titration was continued with the standard acid to pH 4. The color change is from yellow to orange-red.

Next a 2.00 ml aliquot of the solution was pipetted into a 250 ml beaker containing 50 ml deionized water. This solution was neutralized to pH 7.0 with 5 N nitric acid using a pH meter to determine pH. A precipitate of $\text{Zn}(\text{OH})_2$ is formed at pH 7. The solution and precipitate were rinsed from the pH electrodes and the electrodes were removed from the solution. One ml of pH 10 buffer (32 g NH_4Cl plus 285 ml concentrated NH_4OH diluted to 500 ml) was added to the solution. If all of the precipitate did not dissolve, enough buffer was added to just bring it into solution. Deionized water was added to bring the volume to about 125 ml. Three drops of Zincon (2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene) indicator were added and titrated immediately with standard EDTA (ethylene-diaminetetraacetic acid, disodium salt). The end point is a color change from pale blue to yellow.

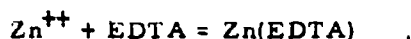
These procedures provide the end-points required to determine the quantities of KOH, K_2CO_3 and ZnO. These quantities are determined by the use of three simultaneous equations. However the reaction stoichiometry must be considered in setting up these equations. The first titration to pH 8 causes the following reactions:



The second titration from pH 8 to pH 4 causes the following reactions:



The third titration of zinc with EDTA may be represented by:



Thus the titration to pH 8 determines all the hydroxide, half the carbonate and half the zincate. The titration from pH 8 to pH 4 determines half the carbonate and half the zincate. The EDTA titration determines all of the zincate which may be expressed in terms of ZnO if desired. The volume of acid required to titrate the hydroxide was obtained by subtracting the volume used between pH 8 and pH 4 from that required to reach pH 8. Thus, $N_{\text{KOH}} = (N_{\text{HNO}_3}) (\text{ml HNO}_3 \text{ to pH 8} - \text{ml HNO}_3 \text{ to pH 4}) / (\text{ml sample})$.

The number of millimoles of zincate was obtained from the EDTA titration: m moles zincate = $5/2 (M_{\text{EDTA}}) (\text{ml EDTA})$. The factor 5/2 is used to convert the millimoles of zincate in a second sample used in the zinc titration to the number in a 5 ml sample since the acid titration used a 5 ml sample. Since four moles of acid react with each mole of zincate in titrating to pH 4, the number of milliequivalents of K_2CO_3 was obtained as follows:

$$\text{meq K}_2\text{CO}_3 = 2 (\text{ml HNO}_3 \text{ from pH 8 to pH 4}) (N_{\text{HNO}_3}) - 4(5/2) (M_{\text{EDTA}}) (\text{ml EDTA})$$

The weight of K_2CO_3 was then:

$$\text{wt K}_2\text{CO}_3 = \frac{0.1382}{2} \text{ meq K}_2\text{CO}_3$$

Finally, the weight of ZnO was:

$$\text{wt ZnO} = 0.08138 (\text{ml EDTA}) (M_{\text{EDTA}}) 5/2$$

Silver. A 5.00 ml aliquot of the solution was pipetted into a 400 ml beaker containing about 150 ml deionized water. The solution was adjusted to pH 3 to 4 with 5 N nitric acid using a pH meter to determine pH. The precipitate of $\text{Zn}(\text{OH})_2$ is redissolved at pH 3 to 4. The solution was rinsed from the pH electrodes after which they were removed from the solution. A silver billet electrode and a salt bridge leading to a saturated calomel reference electrode were placed in the beaker. The agar salt bridge is made with KNO_3 to avoid introducing any anions which would precipitate Ag^+ .

A Beckman model 76 Expanded Scale pH Meter was connected to the silver and reference electrodes. A recorder was also connected to the pH meter. The pH meter was set to permit adequate millivolt change during the analysis. The recorder was set to zero and was used to record the mv changes during the titration.

The solution in the beaker was titrated with a standardized solution of KI. The solution was added incrementally using drop-wise additions as the end point was approached. After each addition, 1/2 minute to 10 minutes were required for the potential to reach a steady value. This variation depended upon the nearness to the end point and also the concentration of Ag in the solution. The millivolt change was recorded. The end point was determined from the potential change per milliliter of solution added, $dE/d\text{ml}$, for each increment. The maximum change per milliliter of solution was the end point. When the end point was not readily determined, a plot of potential as a function of volume added was used to determine the end point.

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| 13. ABSTRACT <p>Electrolytes for sealed silver-zinc batteries have been analyzed for KOH, ZnO, K_2CO_3, and Ag_2O at 025, 0, 25, and 40 C. In such electrolytes the solubility of Ag_2O is of the order of $10^{-6} N$ compared to $10^{-4} N$ in pure KOH electrolytes. The addition of K_2CO_3 while keeping the potassium ion concentration constant decreases the solubility of ZnO. These solutions require about 200 hours to reach steady state conditions.</p> <p>The conductivity of the electrolyte is decreased by the addition of ZnO. When 40 percent KOH is saturated with ZnO its conductivity is decreased to about 80 percent of the conductivity of pure 40 percent KOH. The addition of K_2CO_3 while keeping the potassium ion concentration constant further decreases the conductivity.</p> <p>The density of ZnO-saturated 40 percent KOH solutions shows that the volume of such a solution can be obtained by considering the volumes of solid ZnO and 40 percent KOH to be additive.</p> <p>The freezing points of ZnO-saturated 40 percent KOH solutions containing varying amounts of K_2CO_3 were found to be similar to that of pure 40 percent KOH; namely -37 C. Extreme instances of supercooling were observed in which solidification sometimes did not occur at -65 C.</p> | | |

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|----|---------------------------------|--------|----|--------|----|--------|----|
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| | Zinc oxide, solubility in KOH | | | | | | |
| | Electrolyte Conductivity | | | | | | |
| | Electrolyte freezing point | | | | | | |

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